IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

ANDREAS WINTER ET AL.   :

SERIAL NO: 08/120,105   : ART UNIT: 1713

FILED: SEPTEMBER 10, 1993   : EXAMINER: WILSON

FOR: A PROCESS FOR THE PREPARATION OF   :
      POLYOLEFIN MOLDING COMPOSITIONS
      HAVING A BROAD MELTING RANGE   :

....

Commissioner for Patents
P.O. Box 1450
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APPELLANTS' BRIEF

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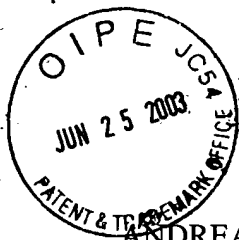P.O. Box 2207
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APPEAL BRIEF

I. THE REAL PARTY OF INTEREST

Basell Polyolefine GmbH is the real party of interest as is stated in Reel

013315, Frame 0977.

II. RELATED APPEALS AND INTERFERENCES

The Board of Appeals on November 30, 1999 mailed the Decision on Appeal

affirming the Examiner that claims 7, 8, 12 and 15 were rejected under 35 U.S.C.§ 102(b)

as anticipated by or in the alternative under 35 U.S.C.§ 103 as being obvious over EP

310734 ("EP '734"). The Board also affirmed the rejection of claims 7, 8, 12 and 15 under

35 U.S.C.§ 103 as being unpatentable over EP 0128046 ("EP '046") and WO 90/03414

("WO '414"). See Paper No. 17 for the Decision on Appeal. The applicants submitted a

Rule 1.132 declaration after the Board's Decision to rebut the obviousness rejections. The

applicants have presented new claims since the time of the Appeal. The Examiner has not

maintained the previous prior art rejections affirmed by the Board of Appeals in view of the

amendments to the claims. The undersigned is not aware of **any current** appeals or interferences involving this application.

III. THE STATUS OF THE CLAIMS

Claims 1-14, 16, 20 and 26 have been cancelled. Claims 15, 17-19, 21-25 and 27-32 are pending and the subject of this appeal.

IV. STATUS OF AMENDMENTS AFTER FINAL

There have been no amendments after final filed.

V. SUMMARY OF THE INVENTION

The invention is directed to a process for the preparation of a polyolefin molding composition comprising at least two polyolefinic components, wherein the composition is characterized by a broad, bimodal, or multimodal melting range in a DSC spectrum determined with a heating/cooling rate of 20° C/min wherein the peak in the melting range has a maximum and can be bimodal or multimodal and the maximum of the peak in the melting range is between 120 and 165°C, the half-intensity width of the melting peak is broader than 10°C and the width determined at quarter peak height is greater than 15°C, wherein such process comprises the direct polymerization of propylene or copolymerization of propylene with olefins of the formula $R^aCH = CHR^b$, in which R^a and R^b are identical or different and are a hydrogen atom or an alkyl radical having 2 to 14 carbon atoms wherein the polymerized ethylene content of the resulting polyolefin composition is from 0 to 2.5% by weight,

to at least two polyolefins of different melting points, wherein the melting points of the

polyolefins must differ by at least 5° C, and wherein the polymerization is carried

out at a temperature of from -60 to 200°C, and a pressure of from 0.5 to 100 bar, in

solution, in suspension or in the gas phase, in the presence of a catalyst, wherein the

catalyst comprises

(A) at least two racemic or s-symmetric metallocenes of the formula (I) as transition-metal

components and an aluminoxane of the formula II and/or formula (III)

or

(B) at least two racemic or s-symmetric metallocenes of the formula (I) as transition-metal

components and a salt-like compound of the formula R_xNH_{4-x} or of the formula

$R_3PHBR'_4$ wherein x is 1, 2 or 3, R is identical or different and is alkyl or aryl, and

R' is aryl, which may also be fluorinated or partly fluorinated. (see claim 17).

VI. REFERENCE APPLIED AGAINST THE CLAIMS

There are currently no references applied against the claims.

VII.   THE REJECTIONS APPEALED FROM IN THE FINAL OFFICE ACTION

1.   Claims 15, 17-19, 21-25 and 27-32 were rejected under 35 U.S.C. § 112,

first paragraph, as containing subject matter which was not described in the specification in

such a way as to reasonably convey to one of skill in the relevant art that the inventor(s) at

the time the application was filed had possession of the claimed invention.

2.   Claims 15, 17-19, 21-25 and 27-32 were rejected under 35 U.S.C. § 112,

second paragraph.

3.   Claim 32 was rejected under 35 U.S.C. § 112, fourth paragraph, for not further specifying a limitation of the subject matter in the parent claim.

4.   Claims 15, 17-19, 21-25 and 27-32 were rejected under the judicially created doctrine of obviousness-type double patenting as being unpatentable over claims of U.S. Patent No. 5,700,886. The applicants filed a terminal disclaimer just prior to the Examiner issuing the Final Office Action. It appears that the terminal disclaimer was not matched with the application when the Examiner issued the Final Office Action. The Examiner has entered the Terminal Disclaimer on Paper No. 48 and this rejection should no longer be applicable.

VIII. THE ISSUES ON APPEAL

1.   Whether the claims are supported in the original specification?

2.   Whether the claims are unpatentable under 35 U.S.C.§ 112, second paragraph?

3.   Whether claim 32 further limits claim 17 since claim 32 requires only a broad melting range while claim 17 requires a broad, bimodal or multimodal melting range?

IX. GROUPING OF THE CLAIMS

Claims 15, 17-19, 21-25 and 27-32 are pending and are the subject of this appeal. These claims do not stand or fall together.

Group I hereinafter refers to claims15, 17-19, 21-25 and 27-31.

Group II hereinafter refers to claim 32.

Again, these claims do not stand or fall together.

X. ARGUMENTS

A. Group I

Claims 15, 17-19, 21-25 and 27-32 were rejected under 35 U.S.C. §112, first and second paragraphs. The claims were objected to as containing new matter. The applicants do not believe that the claims contain new matter. More specifically the Examiner asserts,

"there is no basis in the specification for determining melting ranges from a DSC spectrum using both heating and cooling , i.e., "heating/cooling rates of 20°C/min". The Examiner acknowledges that the specification teaches at page 14, [m]elting points, peak widths, melting ranges and crystallization temperatures were determined by DSC spectrometry (heating/cooling rates of 20°C/min)."

The applicants believe that page 14, lines 16-18 of the specification does teach that melting ranges are determined at heating/cooling rates of 20°C/ min C. This information, together with his knowledge that normally the thermal history is erased to obtain unambiguous material properties, is sufficient for a person of ordinary skill in the art to repeat the measurement.

The language of the present application refers to a "broad, bimodal, or multimodal melting range" and a "melting range maximum". As the applicants previously stated, the definition 2.2 in the right column of page 1 of the previously submitted ISO 3146 (published in 1985, prior to the filing date of this application (see appendix 2)) discloses that a "melting range" is a temperature range, i.e. a temperature interval. A span of temperature can neither have a maximum nor a bimodal or multimodal shape. This is only possible for the curve in this interval. The portion of a DSC curve which departs from the baseline is called "peak" (see definition 13.4 in the left column of page 6 of ISO 3146)

wherein the baseline is the portion or the portions of the DSC curve for which the heat flux is constant or, in other words, which is obtained if the sample does not show a phase transition. Therefore, a person of ordinary skill in the art automatically adds "peak" if he reads "maximum" or "bimodal or multimodal" in the context of a DSC spectrum.

The Examiner, in paragraph 13 of his Office Action mailed September 6, 2002, states:

"a bimodal or multimodal curve would clearly be representative of more

than a single process...".

The applicants respectfully disagree. A bimodal or multimodal curve would <u>clearly be</u> representative of a single process since the term "single process" as used in the note of point 13.4 of ISO 3146 is clearly understood by a person skilled in the art as one source of an exothermic or endothermic process, *e.g.* crystallization or melting (see also point 13.5 of ISO 3146). Further processes with a generation or consumption of heat could be a change of state, a chemical reaction, an adsorption or desorption process, etc. If such a process occurs in parallel to the melting, then it is no longer possible to talk about a "peak" in the sense of ISO 3146.

Since in the present case only one process, *i.e.*, melting occurs, only one "peak" results, which, however, can be bimodal (having two peaks) or multimodal (having several peaks or a shoulder.

With respect to the 35 U.S.C. § 112, second paragraph rejection, claim 17 states that the DSC spectrum is determined with a heating/cooling rate of 20°C which is supported by page 14, lines 16 - 18 of the specification. This means to run first a heating/cooling cycle

and then start recording the DCS curve (see paragraph 17.2.2 in the left column of page 8 of ISO 3146).

The determination of half width and quarter width is in the absence of any further information (as in the present case) only possible, but unambiguous, if the person of ordinary skill in the art follows logic and the pure definition of the ordinary meaning of the terms.

A peak is that portion of a DSC curve which departs from the baseline (definition 13.4 in the left column of page 6 of ISO 3146). The baseline is the portion or the portions of the DSC curve for which the heat flux is constant, i.e. where no phase transition occurs (definition 13.3 of ISO 3146).

Since claim 17 states that the polyolefin molding composition has a melting range there must exist a peak in the DSC spectrum. This peak can be unimodal (broad melting range), bimodal or multimodal, i.e. it can have one, two or more tips. However, since the definition of a peak, in the absence of any further information, can only mean that part of the DSC curve which is between the temperature where the DSC curve leaves the baseline and the temperature where the DSC curve comes back to the baseline again, the whole portion of the DSC curve between these two temperatures is unambiguously the melting peak, independently whether it has one, two or more tips.

At the temperature where the distance, vertical to the temperature axis, between interpolated baseline and the DSC curve is greatest (see definition 13.6 of ISO 3146) is the maximum of the peak in the melting range (which has to be between 120 and 165 °C according to claim 17).

Half width and quarter width are unambiguously determined at a distance from the baseline which is half of the peak height in the maximum or which is a quarter of the peak height in the maximum.

Therefore, it is the meaning of claim 17 is clear, if the melting peak has only one tip or, if it has two or more tips, the valley between the tips is higher than half of the peak height in the maximum. Then half width and quarter widths are the distances between those points where the parallels of the baseline in the respective distances intercept with the DSC curve. For the above reasons, these rejections should be withdrawn.

B. Group II

In addition to the rejections presented in Group I above, claim 32 was also rejected under 35 U.S.C. §112, fourth paragraph as failing to limit a previous claim. Claim 32 depends upon claim 17 and further limits claim 17. Claim 17 can have a melting range that is (a) broad, (b) bimodal or (c) multimodal. Claim 32 requires that the melting range is only a broad melting range. Claim 32 does not require the other two options of a bimodal or multimodal melting range. Therefore claim 32 further limits claim 17. For the above reasons, this rejection should be withdrawn.
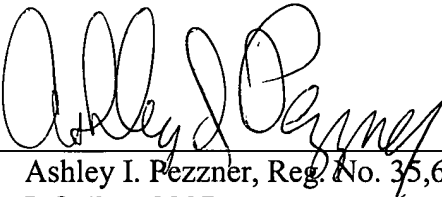
XI. CONCLUSION

It is believed that the claims define an invention which is new, useful, and unobvious. For the above reasons, the applicants request that the Examiner be reversed. This brief is being submitted in triplicate along with a check in the amount of $320.00.

However, in the event that the undersigned is mistaken in his calculations, an appropriate extension of time to respond is respectfully petitioned for, and the

Commissioner is hereby authorized to charge the account of the undersigned attorneys,

Patent Office Deposit Account No. 03-2775, for any fees which may be due upon the filing

of this paper.

Respectfully submitted,

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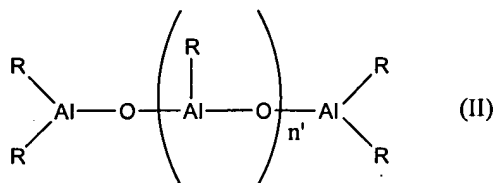   Wilmington, DE 19899
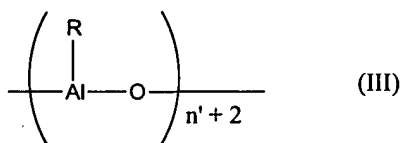   (302) 658-9141

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APPENDIX I

15. The process as claimed in claim 17, wherein the metallocenes are selected from

the group consisting of rac-Me_2Si(2-methyl-1-indenyl)$_2$ZrCl$_2$,

rac-Me_2Si(indenyl)$_2$HfCl$_2$, pheny(methyl)Si(2-methyl-1-inenyl)$_2$ZrCl$_2$,

Me_2Si(2-methyl-4-phenyl-1-indenyl)$_2$ZrCl$_2$, Me_2Si(2-methyl-1-indenyl)$_2$ZrCl$_2$,

Me_2Si(indenyl)$_2$HfCl$_2$, phenyl(methyl)silyl(indenyl)$_2$HfCl$_2$,

rac-ethylene(2-methyl-1-indenyl)$_2$ZrCl$_2$,

rac-Me_2Si(2-methyl-4-phenyl-1-indenyl)$_2$ZrCl$_2$,

rac-ethylidene(2-methyl-4,6-diisopropyl-1-indenyl)$_2$ZrCl$_2$,

rac-Me_2Si(2-methyl-4,5-benzoindenyl)$_2$ZrCl$_2$, dimethylmethylene (9-fluorenyl)

(cyclopentadienyl)ZrCl$_2$,

phenyl(methyl)methylene(9-fluorenyl)(cyclopentadienyl)ZrCl$_2$,

rac-phenyl(methyl)silyl(2-methyl-4,6-diisopropyl-1-indenyl)$_2$ZrCl$_2$,

Ph(Me)Si(2-methyl-4-phenyl-1-indenyl)$_2$ZrCl$_2$,

rac-Me_2Si(2-methyl-4-(1-naphthyl)-1-indenyl)$_2$ZrCl$_2$,

rac-Me_2Si(2,5,6-trimethyl-1-indenyl)$_2$ZrCl$_2$,

rac-Me_2Si(4,5-benzo-1-indenyl)$_2$ZrCl$_2$ and

rac-Me_2Si(4-phenyl-1-indenyl)$_2$ZrCl$_2$.

17. A process for the preparation of a polyolefin molding composition comprising at

least two polyolefinic components, wherein the composition is characterized by a

broad, bimodal, or multimodal melting range in a DSC spectrum determined with

a heating/cooling rate of 20° C/min wherein the peak in the melting range has a

maximum and can be bimodal or multimodal and the maximum of the peak in the

melting range is between 120 and 165°C, the half-intensity width of the melting

peak is broader than 10°C and the width determined at quarter peak height is

greater than 15°C, wherein such process comprises the direct polymerization of

propylene or copolymerization of propylene with olefins of the formula $R^aCH =$

CHR^b, in which R^a and R^b are identical or different and are a hydrogen atom or an

alkyl radical having 2 to 14 carbon atoms wherein the polymerized ethylene

content of the resulting polyolefin composition is from 0 to 2.5% by weight,

to at least two polyolefins of different melting points, wherein the melting points of the

polyolefins must differ by at least 5° C, and wherein the polymerization is carried

out at a temperature of from -60 to 200°C, and a pressure of from 0.5 to 100 bar,

in solution, in suspension or in the gas phase, in the presence of a catalyst,

wherein the catalyst comprises

(A) at least two racemic or s-symmetric metallocenes as transition-metal components and

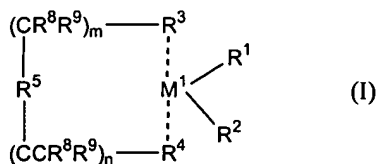an aluminoxane of the formula II

$$
R\!\!\diagdown\!\!\underset{R\diagup}{Al}\!\!-\!\!O\!\!-\!\!\left(\!\!\underset{|}{\overset{R}{Al}}\!\!-\!\!O\!\!\right)_{n'}\!\!\!Al\!\!\underset{\diagdown R}{\overset{\diagup R}{}} \qquad (II)
$$

and/or of the formula III

$$\left(\begin{array}{c} R \\ | \\ -Al-O- \end{array}\right)_{n'+2} \qquad \text{(III)}$$

where in the formulae II and III, the radicals R may be identical or different are a C_1-C_6-alkyl group, a C_1-C_6-fluoroalkyl group, a C_6-C_{18}-aryl group, a C_6-C_{18}-fluoroaryl group or hydrogen, and n' is an integer from 0 to 50, and the aluminoxane component may additionally contain a compound of the formula AlR_3, or

(B) at least two racemic or s-symmetric metallocenes as transition-metal components and a salt-like compound of the formula R_xNH_{4-x} or of the formula $R_3PHBR'_4$ wherein x is 1, 2 or 3, R is identical or different and is alkyl or aryl, and R' is aryl, which may also be fluorinated or partly fluorinated,

where the transition-metal component used comprises at least two metallocenes of the formula I:

$$\begin{array}{c} (CR^8R^9)_m \text{——} R^3 \\ | \qquad\qquad\quad \diagup R^1 \\ R^5 \qquad\qquad M^1 \diagdown \\ | \qquad\qquad\qquad R^2 \\ (CCR^8R^9)_n \text{——} R^4 \end{array} \qquad \text{(I)}$$

in which

M^1 is Zr or Hf,

R^1 and R^2 are identical or different and are a hydrogen atom, a C_1-C_{10}- alkyl group, a C_1-C_{10}-alkoxy group, a C_6-C_{10}-aryl group, a C_6-C_{10}-aryloxy

group, a C_2-C_{10}-alkenyl group, a C_7-C_{40}-arylalkyl group, a C_7-C_{40}-

alkylaryl group, a C_8-C_{40}-arylalkenyl group, or a halogen atom,

R^3 and R^4 are identical or different and are indenyl, cyclopentadienyl or fluorenyl

which are optionally substituted with substituents as defined for R^{11} and

R^{12} and where the substituents are identical or different or form together

with the atoms connecting them a ring,

R^5 is

$$
\begin{array}{c}
R^{11} \\
| \\
- M^2 - \\
| \\
R^{12}
\end{array}
\quad \text{or}
$$

$$
\begin{array}{c}
R^{11} \\
| \\
- C - \\
| \\
R^{12}
\end{array} ,
$$
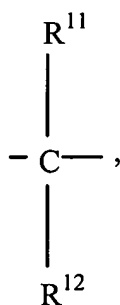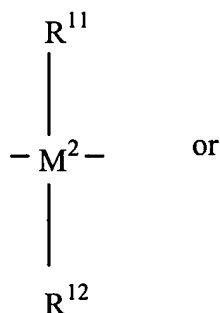
where R^{11} and R^{12} are identical or different and are a hydrogen atom, a halogen

atom, a C_1-C_{10}-alkyl group, a C_1-C_{10}-fluoroalkyl group, a C_6-C_{10}-aryl

group, a C_6-C_{10}-fluoraryl group, a C_1-C_{10}-alkoxy group, a C_2-C_{10}-alkenyl

group, a C_7-C_{40}-arylalkyl group, a C_8-C_{40}-arylalkenyl group or a C_7-C_{40}-

alkylaryl group, or R^{11} and R^{12} together with the atoms connecting them,

form a ring,

M^2 is silicon or germanium,

R^8 and R^9 are identical or different and are as defined for R^{11} and

m and n are identical or different and are zero or 1 and wherein for at least one of

the at least two metallocenes R^3 is a substituted indenyl or an optionally

substituted fluorenyl.

18.   The process as claimed in claim 17, wherein the process comprises the direct

polymerization of propylene or copolymerization of propylene with an olefin

selected from the group consisting of ethylene, 1-butylene, 1-hexene, 4-methyl-1-

pentene, 1-octene and mixtures thereof.

19.   The process as claimed in claim 17, wherein R^1 and R^2 are identical or different

and are a C_1-C_{10}- alkyl group, a C_1-C_{10}-alkoxy group, a C_6-C_{10}-aryl group, a C_6-

C_{10}-aryloxy group or halogen.

21.   The process as claimed in claim 20, wherein said two different metallocenes are

rac-dimethylsilyl(2-methyl-1-indenyl)$_2$ZrCl$_2$ and rac-dimethylsilyl(indenyl)$_2$

HfCl$_2$.

25.   The process as claimed in claim 17, wherein R^1 and R^2 are identical and are

methyl or chlorine,

R^4 and R^3 are indenyl, cyclopentadienyl or fluorenyl, where these ligands may

carry additional substituents as defined for R^{11}.

27.   The process as claimed in claim 17, wherein said metallocenes are chiral

metallocenes.

28.   The process as claimed in claim 25, wherein $-(CR^8R^9)_m-R^5-(CR^8R^9)_n$ is ethylene or CH_3SiCH_3.

29.   The process as claimed in claim 17, wherein M^1 is Zr for all the metallocenes of formula 1.

30.   The process as claimed in claim 17, wherein the polyolefin molding composition is a homo or copolymer with a propylene content of from 97.5 to 100% by weight.

31.   The process as claimed in claim 17, wherein the polyolefin molding composition is a homo polymer of propylene or a propylene ethylene copolymer with an ethylene content of up to 2.5% by weight.

32.   The process as claimed in claim 17, wherein the composition is characterized by a broad melting range.

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APPENDIX 2

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International Standard (ISO) 3146

Plastics — Determination of melting behaviour (melting temperature or melting range) of semi-crystalline polymers

Plastiques — Détermination du comportement à la fusion (température de fusion ou plage de température de fusion) des polymères semi-cristallins

Second edition — 1985-12-15

Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work.

Draft International Standards adopted by the technical committees are circulated to the member bodies for approval before their acceptance as International Standards by the ISO Council. They are approved in accordance with ISO procedures requiring at least 75 % approval by the member bodies voting.

International Standard ISO 3146 was prepared by Technical Committee ISO/TC 61, *Plastics*.

This second edition cancels and replaces the first edition (ISO 3146-1974), of which it constitutes a minor revision.

Users should note that all International Standards undergo revision from time to time and that any reference made herein to any other International Standard implies its latest edition, unless otherwise stated.

INTERNATIONAL STANDARD

Plastics — Determination of melting behaviour (melting temperature or melting range) of semi-crystalline polymers

0 Introduction

The melting behaviour of a crystalline or partly crystalline polymer is a structure-sensitive property.

In polymers a sharp melting point, such as is observed for low molecular mass substances, usually does not occur; instead a melting temperature range is observed on heating, from the first change of shape of the solid particles to the transformation into a highly viscous or viscoelastic liquid, with accompanying disappearance of the crystalline phase, if present. The melting range depends upon a number of parameters, such as molecular mass, molecular mass distribution, per cent crystallinity, and thermodynamic properties.

It may also depend on the previous thermal history of the specimens. The lower or upper limit of the melting range, or its average value, is sometimes conventionally referred to as the "melting temperature".

1 Scope and field of application

This International Standard specifies three methods for evaluating the melting behaviour of semi-crystalline polymers.

Section one specifies a capillary tube method (method A), which is based on the changes in shape of the polymer. This method is applicable to all polymers and their compounds, even if there is no crystalline phase.

Section two specifies a polarizing microscope method (method B), which is based on changes in the optical properties of the polymer.

This method is applicable to polymers containing a birefringent crystalline phase; it may not be suitable for plastics compounds containing pigments and/or other additives which could interfere with the birefringence of the polymeric crystalline zone.

Section three specifies a thermal analytical method (method C), having two variants :

— method C1, which uses Differential Thermal Analysis (DTA);

— method C2, which uses Differential Scanning Calorimetry (DSC).

Both are applicable to all polymers containing a crystalline phase and their compounds.

The melting temperatures determined by the different methods usually differ by several kelvins for the reasons explained in the introduction.

Of the methods given above, experiments have indicated DSC (Differential Scanning Calorimetry) to be the method of choice as having the best reproducibility of results.

2 Definitions

2.1 semi-crystalline polymers : Polymers containing a crystalline phase surrounded by amorphous materials.

2.2 melting range : The temperature range over which crystalline polymers lose their crystallinity when heated.

NOTE — The conventional "melting temperatures" determined by methods A and B are defined in clauses 3 and 8.

1

Section one : Method A — Capillary tube

3 Principle

Heating of a specimen, at a controlled rate, and observation for change in shape.

Reporting of the temperature of the specimen at the first visible deformation as the melting temperature.

NOTE — This method may also be used for non-crystalline materials according to the relevant specifications or by agreement between the interested parties.

4 Apparatus (see figure 1)

4.1 Melting apparatus, consisting of the following items :

a) cylindrical metal block, the upper part of which is hollow and forms a chamber;

b) metal plug, with two or more holes, allowing a thermometer and one or more capillary tubes to be mounted into the metal block a);

c) heating system for the metal block a) provided, for example, by an electrical resistance enclosed in the block;

d) rheostat for regulation of the power input, if electrical heating is used;

e) four windows of heat-resistant glass on the lateral walls of the chamber, diametrically disposed at right angles to each other. In front of one of these windows is mounted an eyepiece for observing the capillary tube. The other three windows are used for illuminating the inside of the enclosure by means of lamps.

NOTE — Other suitable melting apparatuses may be used, provided that they give the same results.

4.2 Capillary tube, of heat-resistant glass, closed at one end.

NOTE — The maximum external diameter should preferably be 1,5 mm.

4.3 Calibrated thermometer, graduated in divisions of 1 K. The thermometer probe shall be positioned in such a way that heat dispersion in the apparatus is not impeded.
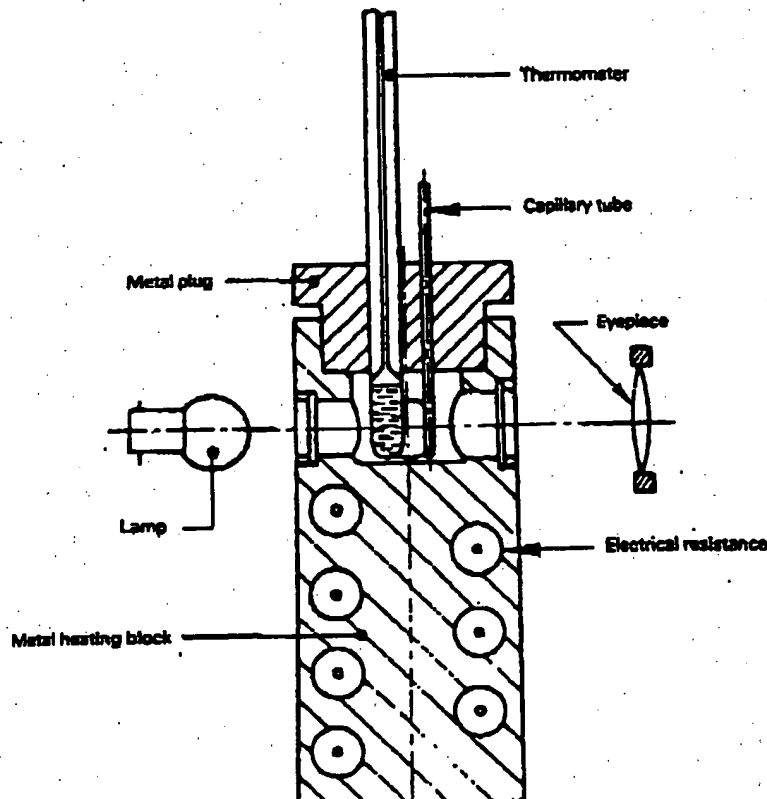

Figure 1 — Apparatus for method A

NOTE — Other suitable temperature-measuring devices may be used.

5 Test specimens

The specimens used shall be representative of the sample of material to be tested.

5.1 Characteristics

Powder of particle size up to 100 μm or cut pieces of films of thickness 10 to 20 μm should preferably be used. Comparison tests shall be carried out on specimens of the same or similar particle size, or similar thickness in the case of layers or films.

5.2 Conditioning

If not otherwise specified or agreed to by the interested parties, the sample shall be conditioned at 23 ± 2 °C and relative humidity of 50 ± 5 % for 3 h prior to the measurement.

6 Procedure

6.1 Calibration

Calibrate the temperature-measuring system periodically over the temperature range used for the test, with reagent grade or certified chemicals.

Chemicals recommended for calibration are listed in table 1.

6.2 Determination

6.2.1 Insert the thermometer (4.3) and the capillary tube (4.2) containing the specimen into the heating chamber (4.1a)] and start the heating. When the temperature of the specimen is about 20 K below the expected melting temperature, regulate the rate of temperature increase to 2 ± 0,5 K/min. Record the temperature at which the specimen begins to change shape.

6.2.2 Repeat the operations specified in 6.2.1 with a second specimen. If the two results obtained by the same operator on the same sample differ by more than 3 K, repeat the procedure on two new specimens.

Insufficient data are available for establishing reproducibility.

Table 1 — Calibration standards

Chemical	Melting temperature[1] (°C)
	42,5
L-Menthol-1	69,0
Azobenzene	76,5
8-Hydroxyquinoline	80,2
Naphthalene	96,0
Benzyl	113,5
Acetanilide	121,7
Benzoic acid	126,0
Phenacetin IN (4-ethoxyphenyl) acetamide]	151,5
Adipic acid	158,4
Indium	165,7
Sulfanilamide	170,3
Hydroquinone	169,5
Succinic acid	208,0
2-Chloroanthraquinone	217,0
Anthracene	223,4
Saccharin	231,3
Tin	247,0
Tin(II) chloride	261,5
Phenolphthalein	

1) The temperatures indicated refer to theoretically pure chemicals; the values of the actual melting point for the standard materials used should be certified by the supplier.

7 Test report

The test report shall include the following information :

a) reference to this International Standard;

b) reference of the method used (method A);

c) complete identification and description of the material tested;

d) shape and size (or mass) of the specimens;

e) previous thermal history of the specimens;

f) conditioning;

g) heating rate;

h) temperatures, in degrees Celsius or in kelvins, of two successive individual measurements, and their arithmetic mean;

i) any operational details not specified in this International Standard or regarded as optional, as well as any incidents liable to have affected the results.

Section two : Method B — Polarizing microscope

8 Principle

Heating of a specimen, positioned between the polarizer and analyser of a microscope, at a controlled rate.

Measurement of the temperature at which the crystalline polymer loses its optical anisotropy, as detected by the disappearance of birefringence, as the melting temperature.

9 Apparatus

Ordinary laboratory apparatus and

9.1 Microscope, with a disk polarizer and a cap analyser, or a polarizing microscope with built-in analyser, with magnification from X 50 to X 100.

9.2 Micro hot-stage, consisting of an insulated metal block that can be mounted slightly above the microscope stage. This block shall be

a) provided with a hole for light passage;

b) electrically heated, with adequate controls for adjustment of heating and cooling rates;

c) constructed to provide a chamber with a heat baffle and a glass cover, for carrying out measurements in an inert atmosphere;

d) provided with a hole for insertion of a temperature-measuring device near the light hole.

9.3 Thermometers, calibrated, or equivalent temperature-measuring devices, for the test temperature ranges.

10 Test specimens

10.1 Powdered materials

Place a 2 to 3 mg portion of the powder (particle size not more than 100 μm) on a clean slide and cover with a cover glass.

Heat the specimen, the slide and the cover on a hot-plate slightly above the melting temperature of the polymer. By a slight pressure on the cover glass, form a thin film of thickness 0,01 to 0,04 mm and allow it to cool slowly by switching off the hot-plate.

10.2 Moulded or pelleted materials

Cut from the sample, with a microtome, a film of thickness approximately 0,02 mm, place it on a clean slide and cover with a cover glass. Heat and melt it as specified in 10.1.

10.3 Film or sheet materials

Cut a 2 to 3 mg portion of the film or sheet, place it on a clean slide, cover with a cover glass and proceed as specified in 10.1.

NOTE — The preliminary melting of the specimens between slide and cover presents the advantage of destroying any birefringence due to orientation or internal stresses, and also of reducing the danger of oxidation during the test. The need for an inert gas stream — as described in 11.2 — is thus limited to very special cases. The reproducibility of the measurements is also increased. However, by agreement between the interested parties, the determination may be carried out directly on the powder or cut film piece without preliminary melting. This deviation should be stated in the test report.

10.4 Conditioning

See 5.2.

11 Procedure

11.1 Calibration

See 6.1.

11.2 Determination

Place the glass microscope slide with the specimen on the micro hot-stage (9.2). Adjust the light source to maximum light intensity and focus the microscope (9.1).

For specimens that are degradable by air, adjust the gas inlet to the stage so that a slight stream of inert gas blankets the stage, keeping it under slight positive pressure to prevent ingress of air. Rotate the analyser to obtain a dark field; the crystalline material will appear bright on a dark field. Adjust the controller to heat the stage gradually (at a rate not higher than 10 K/min) to a temperature that is lower than the melting temperature, θ_m, as determined approximately by previous test, by the following amounts :

10 K for θ_m < 150 °C

15 K for 150 °C < θ_m < 200 °C

20 K for θ_m > 200 °C

Then adjust the controller so that the temperature rises at a rate of 1 to 2 K/min.

Observe the temperature at which birefringence disappears, leaving a totally dark field. Record this temperature as the melting temperature of the sample.

Turn off the heating and remove the glass cover, heat baffle and specimen slide.

Repeat the procedure with another specimen. If the two results obtained by the same operator on the same sample differ by more than 1 K, repeat the procedure on two new specimens.

According to the results of round robins, the repeatability was 2 K. Insufficient data are available for establishing reproducibility.

12 Test report

The test report shall include the following information :

a) reference to this International Standard;

b) reference of the method used (method B);

c) complete identification and description of the material tested;

d) shape and size (or mass) of the specimens;

e) previous thermal history of the specimens;

f) conditioning;

g) description of preliminary heating on the slide, if applicable;

h) presence and type of inert gas, if applicable;

i) heating rate;

j) temperatures, in degrees Celsius or kelvins, of two successive individual measurements and their arithmetic mean;

k) any operational details not specified in this International Standard or regarded as optional, as well as any incidents liable to have affected the results.

Section three : Method C — Thermal analysis (DTA or DSC)

13 Additional definitions

13.1 Differential Thermal Analysis; DTA :[1] A technique in which the temperature difference between a substance and a reference material is measured as a function of temperature while the substance and reference material are subjected to a controlled temperature programme.

NOTE — The record is the differential thermal or DTA curve; the temperature difference, ΔT, should be plotted on the ordinate with endothermic reactions downwards and temperature, T, or time, t, on the abscissa, increasing from left to right.

13.2 Differential Scanning Calorimetry; DSC :[1] A technique in which the difference in energy inputs into a substance and a reference material is measured as a function of temperature while the substance and reference material are subjected to a controlled temperature programme.

NOTE — Two modes, power-compensation differential scanning calorimetry and heat-flux differential scanning calorimetry, can be distinguished, depending on the method of measurement used.

13.3 baseline :[2] The portion or portions of the DTA or DSC curve for which ΔT or the heat flux is approximately constant (approximately zero in DTA).

For example, see AB and DE in figure 2.

13.4 peak :[2] That portion of a DTA or DSC curve which departs from, and subsequently returns to, the baseline.

For example, see BCD in figure 2.

NOTE — A peak is attributable to the occurrence of some single process. It is normally characterized by a deviation from the established baseline, a maximum deflection, and a re-establishment of a baseline, not necessarily identical to that before the peak.

13.5 endothermic peak; endotherm :[2]

(1) In DTA, a peak where the temperature of the sample falls below that of the reference material; that is ΔT is negative. (The melting phenomenon is an endothermic change.)

(2) In DSC, a peak where the energy input to the sample is larger than that to the reference material.

13.6 peak height :[2] The distance, vertical to the temperature axis, between the interpolated baseline and the peak tip.

For example, see CF in figure 2.

NOTE — There are several ways of interpolating the baseline; that shown in figure 2 is only an example. Locations of points B and D depend on the method of interpolation of the baseline. Other examples of interpolation of the baseline are shown in figure 3.

13.7 peak area :[2] The area enclosed between the peak and the interpolated baseline(s). (See the note to 13.6.)

For example, see BCDB in figure 2.

13.8 extrapolated onset temperature :[2] The temperature determined by the point of intersection of the tangent drawn at the point of greatest slope on the leading edge of the peak (for example, tangent t in figure 2) with the extrapolated baseline (for example BG in figure 2).

For example, see G in figure 2, and figure 3.

NOTE — For polymers having a wide melting range, the extrapoled onset temperature indicates the initial point of the rapid rise of the melting curve, but not necessarily the initial melting.

13.9 peak temperature :[2] The temperature at the time at which the differential temperature or heat flux during that peak has the maximum value.

For example, see C in figure 2.

13.10 sample :[2] The actual material to be tested, whether diluted with an inert material or undiluted.

13.11 specimens :[2] Portions of the sample to be tested and the reference material.

13.12 reference material :[2] A substance known to be thermally inactive over the temperature range of interest, for example α-aluminium oxide (α-Al_2O_3).

13.13 sample holder :[2] The container or support for the test portion of the sample.

13.14 reference holder :[2] The container or support for the reference material.

13.15 specimen holder :[2] The complete assembly in which the specimens are housed. When the heating or cooling source is incorporated in one unit with the containers or supports for the sample and reference material, this is regarded as part of the specimen-holder assembly.

13.16 block :[2] A type of specimen-holder assembly in which a relatively large mass of materials is in intimate contact with the specimens or specimen holders.

1) Definition taken from : Nomenclature Committee of the International Confederation for Thermal Analysis. Nomenclature in thermal analysis : Part IV. J. Thermal Anal. 13 1978 : 387-392.

2) Definition taken from : Nomenclature Committee of the International Confederation for Thermal Analysis. Nomenclature in thermal analysis : Part II. Talanta 19 1972 : 1079-1081.

13.17 differential thermocouple: ΔT thermocouple : [1]
The thermocouple system used to measure temperature or heat-flux differences.

14 Principle

Heating of a sample and an appropriate reference material at a controlled rate in a suitable DTA (method C1) or DSC (method C2) apparatus.

Recording of a DTA or DSC curve from which one or several characteristic points, related to the melting behaviour, are determined.

15 Apparatus

15.1 Differential thermal analyser or differential scanning calorimeter.

Most commercially available and custom-built instruments may be used.

The principal design characteristics of such instruments are

a) a heated block with two holders for the specimens identically positioned and guaranteeing the same heat transfer conditions for both;

b) a temperature-recording system;

c) an electrical heater in the block or a furnace with adequate controls for adjustment of heating rate to linear conditions within ± 0,5 K/min.

Synchronous recordings of the DTA curve and the temperature difference ΔT shall permit temperature recording with a sensitivity not less than 2 K per millimetre on the recorder scale.

The DSC apparatus is constructed similarly to the DTA apparatus but with separate compensating devices for the two specimen holders and with electronic equipment maintaining the temperatures of the specimens of the sample and reference material at the same level by variation of the required power input.

The peak area shall be not less than 2 cm²; the peak height shall be at least 10 times the height of the noise level.

15.2 Thermocouples, rigidly fixed in the specimen compartments, possessing identical characteristics within the graduation precision limits.

15.3 Equipment for filling the specimen containers with inert gas, or for passage of a constant measured flow of inert gas through the containers.

16 Test specimens

16.1 Characteristics

Recommended specimens are given in table 2.

Since milligram quantities of material are used, it is essential to ensure that the specimens are homogeneous and representative.

Table 2 — Characteristics of test specimens

Sample form	Particle size	Mass of test portion
Powder	diameter : up to 0,5 mm	
Cut film	thickness : 0,05 to 0,50 mm area : 0,25 to 4,00 mm²	up to 50 mg
Fibre	diameter : up to 0,50 mm length : up to 2,00 mm	

NOTE — Since the results are affected by the mass of the specimen and by the particle size and shape, the specimens to be compared should have approximately the same particle size and shape and the same mass.

16.2 Conditioning

See 5.2.

17 Procedure

17.1 Calibration

Calibrate the temperature measuring system periodically over the temperature range used for the test.

Certified reference materials are available and are listed in table 3.

Table 3 — DTA reference materials for transition temperatures in the range 125 to 435 °C

Reference material[1]	DTA mean values, (°C)	
	Extrapolated onset temperature, T_o	Peak temperature, T_p
Potassium nitrate	128	135
Indium metal	154	159
Tin metal	230	237
Silver sulfate	424	433

1) ICTA-NBS Certified Reference Materials for Differential Thermal Analysis, available from the US National Bureau of Standards, Washington, DC 20234, USA. The indicated values refer only to a specific certified batch.

NOTE — The characteristic points (T_o and T_p) are not to be confused with the true melting temperatures as reported in the literature.

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1) Definition taken from : Nomenclature Committee of the International Confederation for Thermal Analysis. Nomenclature in thermal analysis : Part II. *Talanta* 19 1972 : 1079-1081.

17.2 Determination (methods C1 and C2)

17.2.1 Weigh the specimen into the sample holder of the instrument (15.1) immediately after removal of the sample from the conditioning area. If applicable, start the passage of a stream of an inert gas (freed from oxygen and dried, for example by bubbling through an alkaline pyrogallol solution) through the sample holder. Operate the instrument according to the manufacturer's instructions. The maximum temperature recorded shall be at least 50 K above the peak temperature. The recommended heating rate is 10 K/min.

From the DTA or DSC curve recorded during this first thermal cycle, determine the melting behaviour of the material "as received", which may include thermal memories from the manufacturing process.

17.2.2 If it is desired to erase the effects of the previous thermal history of the specimen in order to obtain an unambiguous material identification, a second thermal cycle shall be performed, as follows:

— at the end of the first cycle, hold the specimen under inert gas atmosphere, about 30 K above the melting peak (T_p) for 10 min, then cool it at a rate of 10 K/min to 50 K below the peak crystallization temperature;

— immediately repeat the heating cycle at a rate of 10 K/min and record the heating curve.

18 Expression of results

The following values, in degrees Celsius or in kelvins, are read from the endothermic DTA or DSC curves recorded by the instrument :

a) T_o: extrapolated onset melting temperature;

b) T_p: peak melting temperature.

According to the results of a round robin carried out in 1984, the repeatability was within 2 K and the reproducibility within ?.

19 Test report

The test report shall include the following information :

a) reference to this International Standard;

b) reference of the method used (method C1 or C2);

c) complete identification and description of the material tested;

d) shape and size (or mass) of the specimens;

e) previous thermal history of the specimen;

f) conditioning;

g) kind of instrument used;

h) type of the sample holder (including its shape, material, etc.);

i) type of temperature-measuring system (including type of thermocouple);

j) location of the temperature-measuring system (inside or outside the sample holder);

k) kind, size and form of the reference material;

l) if necessary, composition and physical parameters (pressure, flow rate, moisture content, etc.) of the inert gas;

m) heating rate;

n) onset temperature T_o and peak temperature T_p in degrees Celsius or in kelvins, of the endothermic curve representing the initial and final melting temperatures, respectively, of the sample, both corrected by the calibration data; the results of both thermal cycles shall be reported; if not otherwise specified, the reference results are those of the second cycle;

o) any operational details not specified in this International Standard or regarded as optional, as well as any incidents liable to have affected the results.
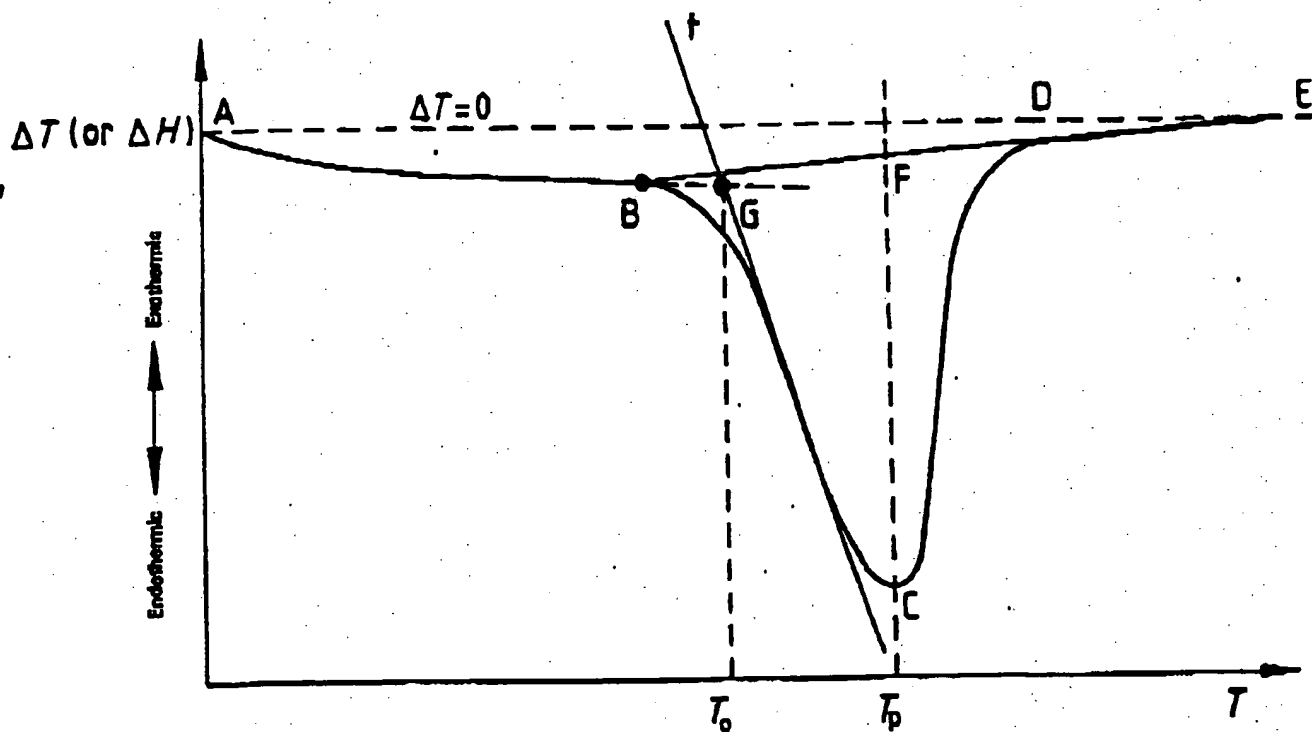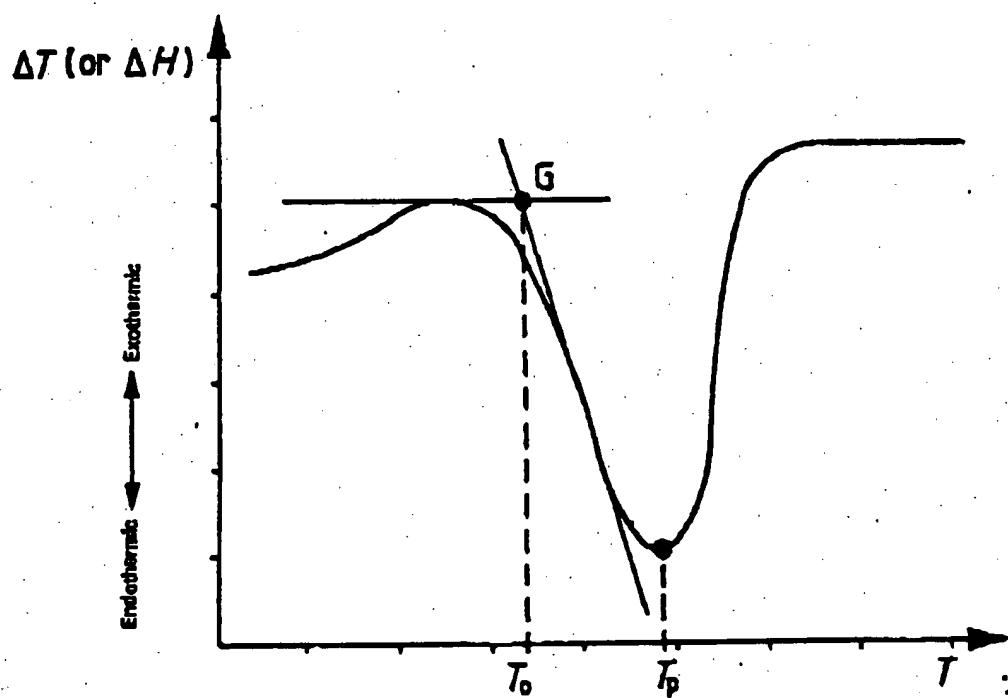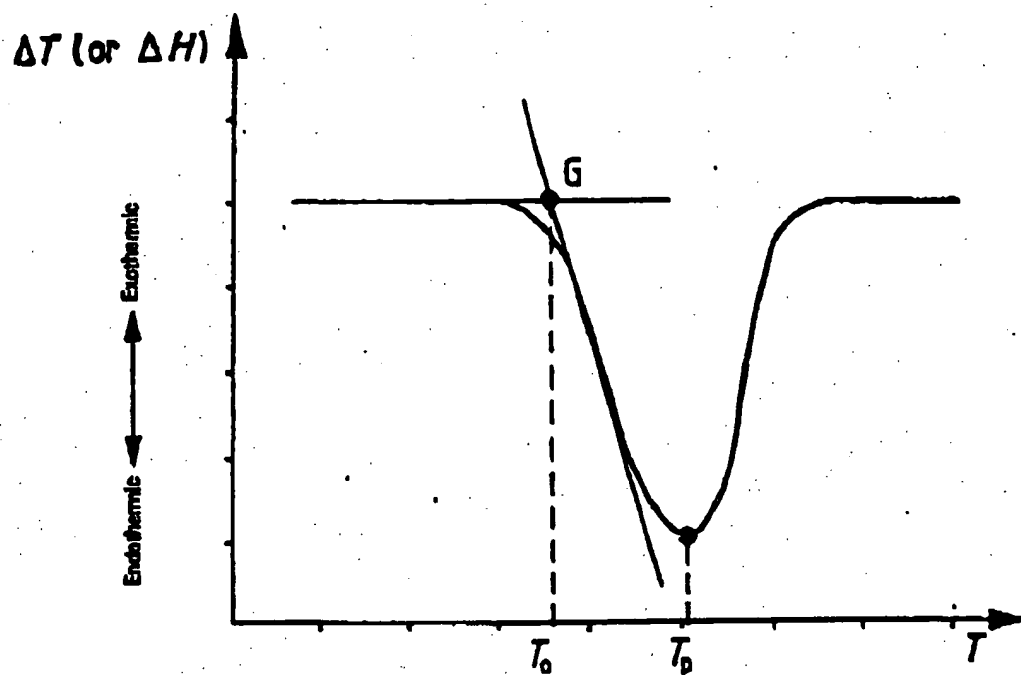
Figure 2 — Formalized DTA (or DSC) curve

T_o: Extrapolated onset temperature

T_p: Peak temperature

Figure 3 — Examples of evaluation of T_o and T_p on DTA (or DSC) curves